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LAWRENCE LIVERMORE NATIONAL LABORATORY

Sub-Scale Prototype Spent Nuclear Fuel/High Level Waste (SNF/HLW) Containers - B559010 REV 02

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Final Report
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ACRONYMS

DOE	U.S. Department of Energy
DSO	Defense Science Office
SNF	spent nuclear fuel
HLW	high level waste
HPCRM	high performance corrosion-resistant material
LLNL	Lawrence Livermore National Laboratory
RPM	revolutions per minute

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1. PURPOSE

The purpose of this portion of the project was to demonstrate the feasibility to coat large structures with amorphous metallic glass materials. In total, three sub-scale models of SNF/HLW containers will be fabricated from Type 316L stainless steel and coated with SAM1651 or an acceptable SAM2X5 powder (completely amorphous) if available. As of this report, one prototype container has been sprayed with a coating thickness of 2 mm. A second container has been sprayed on the outer diameter only to a coating thickness of 1 mm. Both containers have been coated with SAM1651 material.

Each sub-scale model of SNF/HLW container has a length of 2235 mm (88 inches) and a diameter of 762 mm (30 inches). The containers were fabricated by Douglas Brothers of Portland, ME, as a rolled and welded product from Schedule 10S Type 316L. The containers were supplied with one end welded in place and lids provided for closure after spraying and have a total weight of approximately 657 kg (1446 pounds) each without the bottom and closure lid.

Completion of the second prototype and the spraying of the third prototype have been suspended pending availability of additional SAM1651 powder. Some of the available SAM1651 powder has been used to spray initial qualification samples for corrosion testing by other HPCRM team members.

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2. SPRAY PROCEDURE

2.1 HIGH VELOCITY OXYGEN-FUEL PROCESS

The high velocity oxygen-fueled (HVOF) process was used for spraying of the prototype containers. The torch used was a TAFA Model 5220 with a 100 mm barrel length. Specific torch parameters used to spray the containers are listed in Table 2-1.

Table 2-1. Parameter aim settings and actuals used for grit blast and spray of containers and initial qualification samples.

Spray Parameter	**Containers and Qualification Samples**		**Qualification Samples Only**	
	Aim Setting, SAM1651	**Actual, SAM1651**	**Aim Setting, SAM2X5**	**Actual, SAM2X5**
Oxygen Flow, l/min	897	897 +/- 1%	873	873 +/- 1%
Kerosene Fuel Flow, l/hr	28.4	28.4 +/- 1%	25.7	25.7 +/- 1%
Barrel length, mm	100	100	100	100
Powder carrier gas flow, l/min (N2)	10	10 +/- 1%	10	10 +/- 1%
Powder feed rate, gm/min	75	75 +/- 5%	75	75 +/- 5%
Spray distance, mm	330	330 +/- 5%	330	330 +/- 5%
Surface speed (container OD), m/min	120	120 +/- 5%	120	120 +/- 5%
Torch traverse (container OD), mm/rev	6	+/- 0.2%	6	+/- 0.2%
Torch speed (container end), mm/min	1500	+/- 0.2%	1500	+/- 0.2%
Raster step (container end), mm	6	+/- 0.2%	6	+/- 0.2%
Maximum substrate temperature, C	150	198	150	198
Average substrate temperature, C	Less than 150	171	-	171
Grit Blast Parameter				
Initial substrate roughness	>6 micron Ra	9.81 +/- 0.68	>6 micron Ra	9.81 +/- 0.68
Blasting surface speed (container OD), m/min	5.5	+/- 5%	5.5	+/- 5%
Blast nozzle traverse (container OD), mm/rev	23	+/- 0.2%	23	+/- 0.2%
Blast nozzle speed (container end), mm/min	192	+/- 0.2%	192	+/- 0.2%
Raster step (container end), mm	12	+/- 0.2%	12	+/- 0.2%

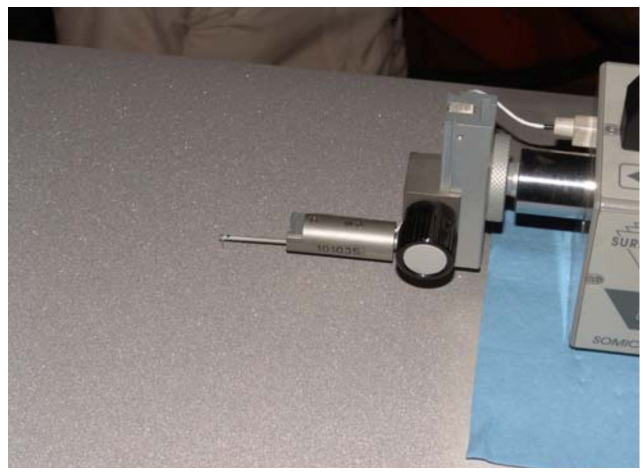
2.2 SPRAY PROTOCOL

The spray protocol used for the SAM1651 material limited the time of continuous spray to one hour, at which time the barrel of the torch was changed. Prior experience with SAM1651 as well as the initial spraying work in this project indicated that shortly after 1 hour the barrel would clog with powder. This is thought to be due to the wearing of the inner diameter (ID) by the powder flow causing a higher surface roughness which then allowed the semi-molten particles to adhere to the ID.

The surface speed used for spraying of the prototype containers was selected based upon the maximum rotation speed at which the containers could be safely rotated. Due to the out-of roundness as well as the height of the weld bead of the fabricated container, only 50 RPM rotation speed could be used. For the 762 mm diameter container, the 50 RPM rotation speed resulted in a surface speed for spraying of 120 meters per minute (m/min). This limited the spray rate used to the 75 gm/min rate in order to keep the application rate of the material to less than 12 micron per pass.

For the initial surface preparation, the surface area was limited to that which could be grit blasted within a 30 minute time period in order to minimize the time between the end of blasting and the start of spraying. This resulted in three sections being blasted and sprayed per container on the outer diameter. Prior to spraying each section after blasting, the surface roughness was measured using a stylus instrument, Figure 2.2-1. A minimum of eight measurements were taken for each blast section and the average reported in Table 2-1. Each section was approximately 1/3 the container length. Approximately 200 mm of length was not coated with the rest of the OD and was left to be coated with the end face. After completion of the OD length and the first end, the lid was welded onto the container and the final end sprayed.

(a)



(b)

Figure 2.1-1. A portable stylus surface profilemeter was used to meaure the roughness of each grit blasted section.

The substrate temperature was measured using optical pyrometers with spectral response of 8-14 um. The surface of the coating on the containers was the target for the pyrometer. An emissivity setting of 0.95 was used. Maximum temperatures were measured approximately 50 to 75 mm behind the torch during spraying. The maximum temperature in Table 2-1 was recorded during spraying of the lid end (container totally closed) and was only recorded for 1-2 minutes. The average temperature in Table 2-1 is for the final 0.5 mm of coating thickness. The maximum and average substrate temperatures were higher than desired due to the amount of air cooling available that was spread over the large surface area of the container. This maximum temperature limit was developed for carbide type materials and to date no adverse affects on the SAM materials has been noted due to higher temperatures (+50 to 75 ºC). Therefore, in order to have as continuous of spray cycle as possible, the higher substrate temperatures were allowed.

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3. AMORPHOUS POWDERS

Four 125 kg heats of material were made by Carpenter Specialty Powder in order to determine the atomization parameters required to produce powders with good flow characteristics. These lots were run through the powder feeder to determine if they would flow continuously without the torch running. Three of the four lots were determined to flow continuously, Table 3-1.

Table 3-1. Powder flow test results of the four 125 kg heats of powder which indicated problems with only one lot of material.

Powder	ID	Lot#	Flow Results
Sam1651	Sam-001	130658	Powder flowed at set point 1 hour
Sam1651	Sam-002	130659	No steady flow at any time
Sam1651	Sam-003	130660	Powder flowed at set point 1 hour
Sam1651	Sam-004	130661	Powder flowed at set point 1 hour

From these results, atomization parameters were chosen to produce three production heats of the SAM1651 material. Each heat was 900 kg of atomized powder prior to sizing into acceptable distributions for spraying. The quantities within –58+15 micron size range for the three heats of material with chemistries are given in Table 3-2.

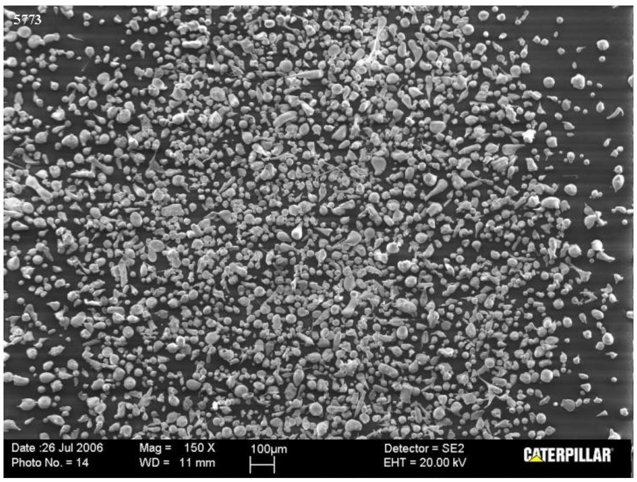
Table 3-2. Powder quantities and reported chemistries of production lots of SAM1651.

	lbs delivered	Screened Particle Size, micron	B	C	Cr	Mo	Y	Fe
V5773	285	-58+15	1.29	3.90	15.00	25.80	3.20	bal
V5774	291	-58+15	1.32	3.70	15.10	25.90	3.00	bal
V5793	397	-58+15	1.28	3.60	15.30	25.50	3.80	bal

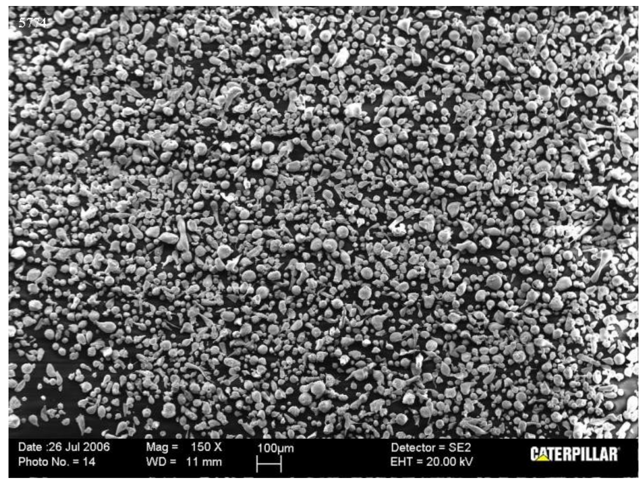
The V5773 and V5774 lots flowed well enough to allow for approximately 5 kg of material to be loaded into the powder hopper and sprayed for one hour. It was found that putting more than 5 kg of material in the hopper could result in erratic flow rates. This was attributed to bridging of the powder within the hopper above the hole through which the powder was metered. The flow of the V5973 lot was similar to the V5773 and V5774 lot but this material would plug the metering hole in the powder feeder after ~1-3 lbs of material had been sprayed.

SEM examinations of the powder to compare the V5773, V5774, and V5973 lots indicated that the powder morphology of the three lots of material were similar but all still have numerous acicular particles that can be detrimental to the flow of the powder, Figures 3-1 and 3-2. After discussion with Carpenter, the V5793 lot was returned for additional screening in an attempt to reduce the amount of acicular material. The V5793 lot contained a high quantity of acicular particles that would plug the hole in the powder pickup shaft used to meter the powder into the carrier gas stream. This lot was returned to Carpenter where it was re-screened through the same coarse 58 micron screen. This double screening removed an additional amount of the acicular or fiber particles that plugged the powder pickup shaft, Figure 3-3. Flow of the V5793 lot was acceptable after the re-screening. Additional work is planned to further characterize the powder morphology of the different lots of the SAM1651.

For the qualification samples produced, the high boron content SAM material used was SAM2X5, lot 06-015.



(a)



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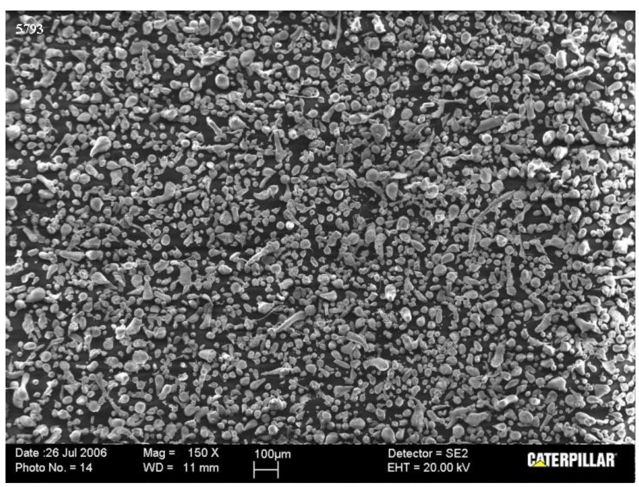
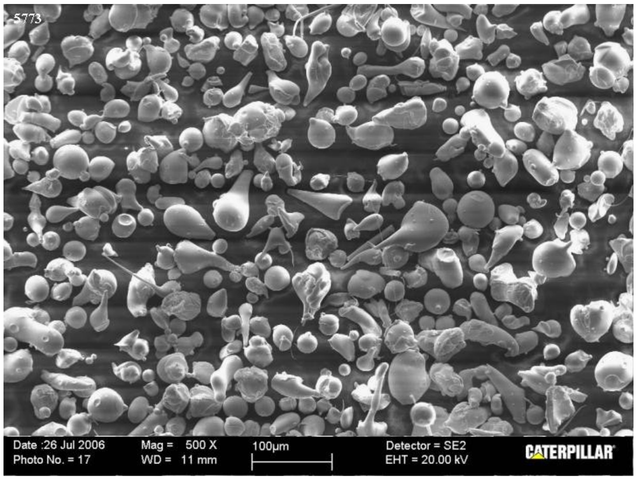


(c)

Figure 3-1 Low magnification scanning electron microscope photos of the three lots of SAM1651 material used for coating the prototype containers, V5773 (a), V5774 (b), and V5793 (c).



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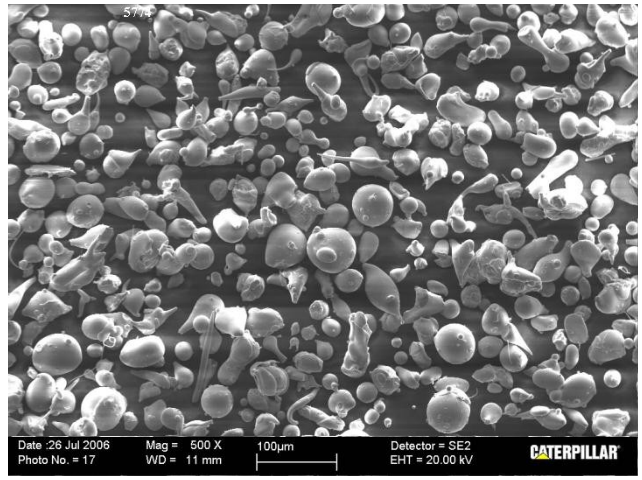

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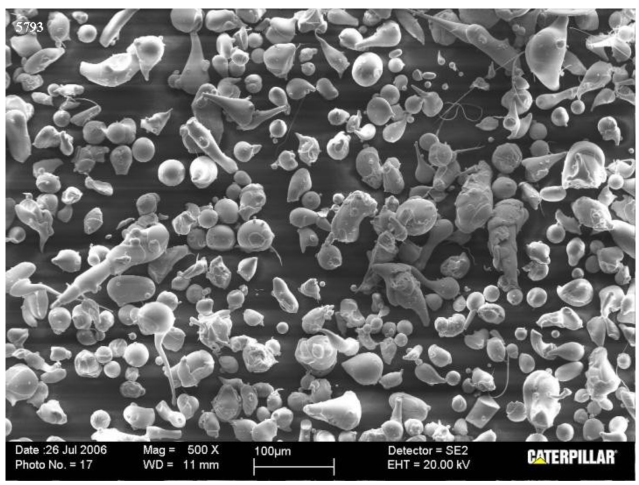

(c)

Figure 3-2 High magnification scanning electron microscope photos of the three lots of SAM1651 material used for coating the prototype containers, V5773 (a), V5774 (b), and V5793 (c).

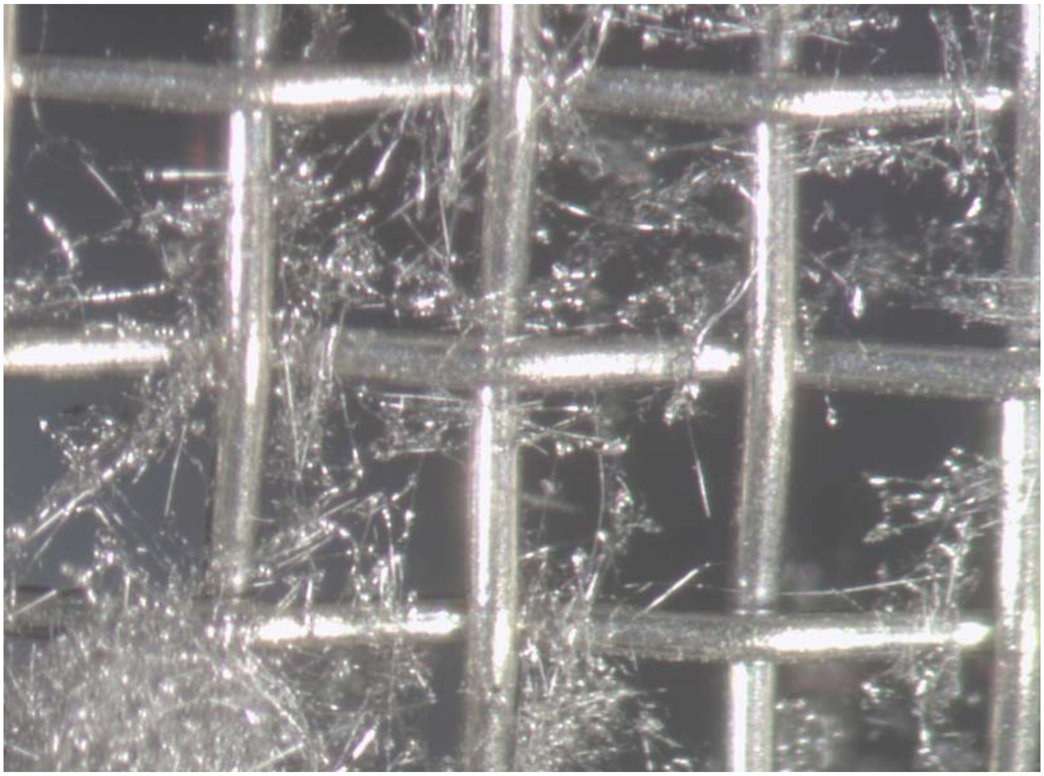

Figure 3-3 32x picture of fiber strands found in powder hopper screens after multiple fills of the powder hopper without clean out. SAM1651 powder, lot V5793, previously rescreened through 58 micron screen at Carpenter.

3.1 CRYOMILLING

In an effort to more fully utilize the powder produced, cryomilling of the off-sized powder (larger than 53 micron) was investigated to determine if this method could be use to economically produce powder of better powder morphology, the correct particle size and amorphous structure. Pittsburgh Materials Technologies was the source used for cryomilling. The milling of the powder is down in at liquid nitrogen cooled chamber with a nitrogen atmosphere using a “recipe” provide by University of California-Davis. The low milling temperature reduces the chance for the material to heat and crystallize.

Sample runs were made using existing milling chambers. The units were for research purposes and therefore held small quantity of material. Samples were processed for 10, 20, 30 and 40 minute milling times. The resulting particle size ranges of the milled material are shown in Figure 3.1-1. The method would be capable of provide a particle size range for spraying.

Due to the small size of the existing milling chamber, the majority of the cost to mill the existing material would be the labor to load and unload. Pittsburgh Materials estimated cost for this to be ~$120 per lb of material milled (not material yield). This was determined not be cost effective for the current material and work on cyromilling was stopped. If large milling units that are commercially available were to be used, Pittsburgh Materials believed that they could mill material for under $15 per lb. Further work to understand the actually yield of powder with the correct size distribution for spraying would be needed as well as determining the characteristics of the coating produced with this type of powder. At this time, recycling of the oversized material via re-melting at the original powder manufacturer appears to be the best approach to reduce powder cost.

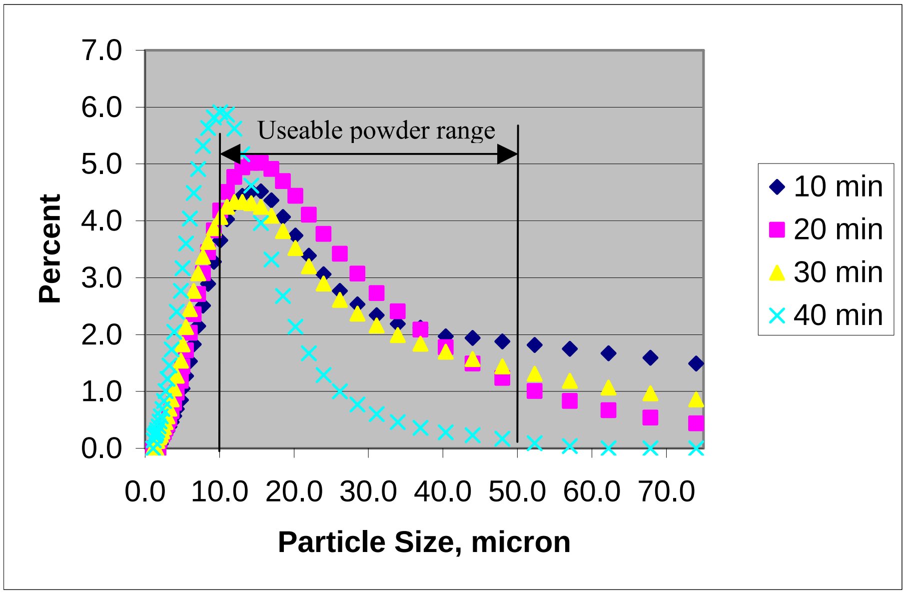

Figure 3.1-1. Powder size distribution of cyromilled powdered after 10, 20, 30 and 40 minute milling times are shown. The amount of material in the useable range would need to be increased for this process to be economical.

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4. CONTAINERS AND INITIAL QUALIFICATION SAMPLES

Due to the non-uniform diameter of the fabricated containers, it was not possible to mount the containers in the lathe chuck for turning. A rolling fixture was designed and fabricated to allow the container to be rotated at a speed of up to 50 RPM for spraying, Figure 4-1.

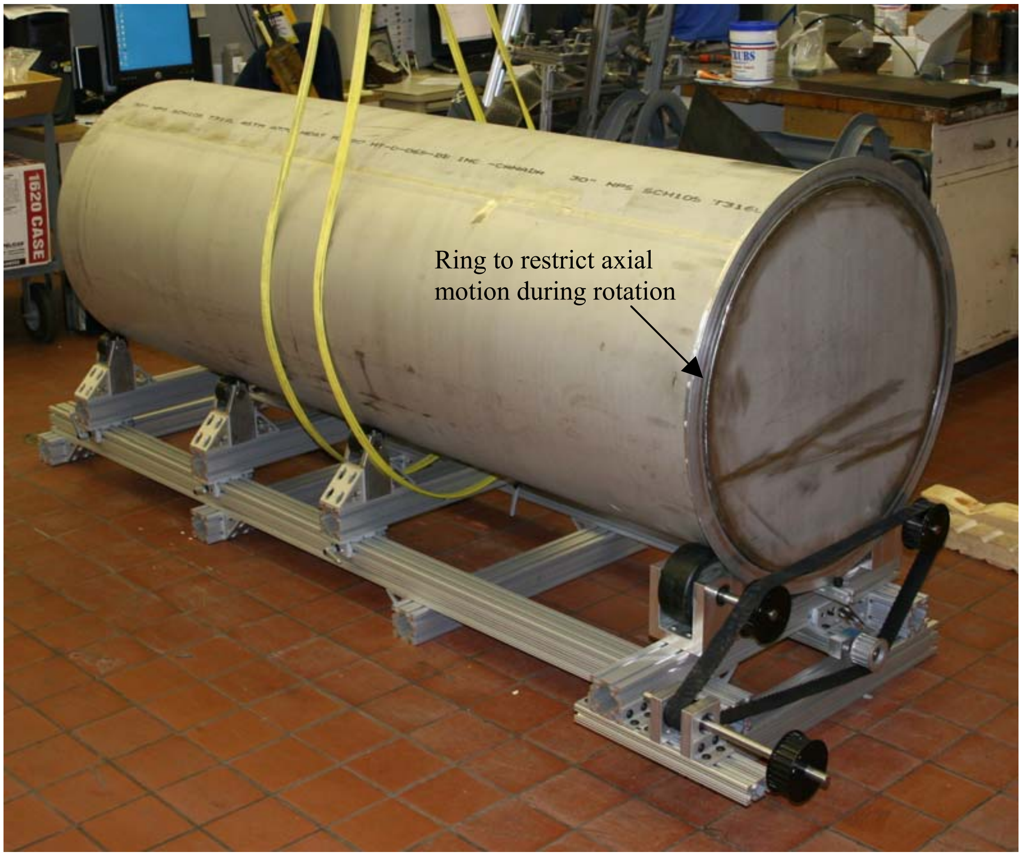


Figure 4-1. Prototype container mounted on the rolling fixture used for spraying. Note ring that was mounted on the end to restrict the axial motion of the container during rotation.

4.1 CONTAINER 1

Spraying of the first prototype container started on July 17, 2006. The OD of the container is the first surface to be sprayed with the ends to follow. Initially, the OD length was divided into three sections that would allow for each section to be grit blasted within 30 minutes to prevent the blasted surface from being exposed for longer time than this. Each section was then initial sprayed to ~200 microns thickness, Figure 4.1-1. After completion of each section (blast and spray), the full length was sprayed continuously for one hour which resulted in an additional ~200 microns being applied for each hour of spraying, Figure 4.1-2. Continuous spraying was limited to one hour intervals by two main factors, 1) the amount of powder that could be loaded into the powder feeder with cause feed problems and 2) the torch barrel life. The torch barrel life is thought to be due to the inner diameter (ID) of the torch barrel being worn by the flow of the

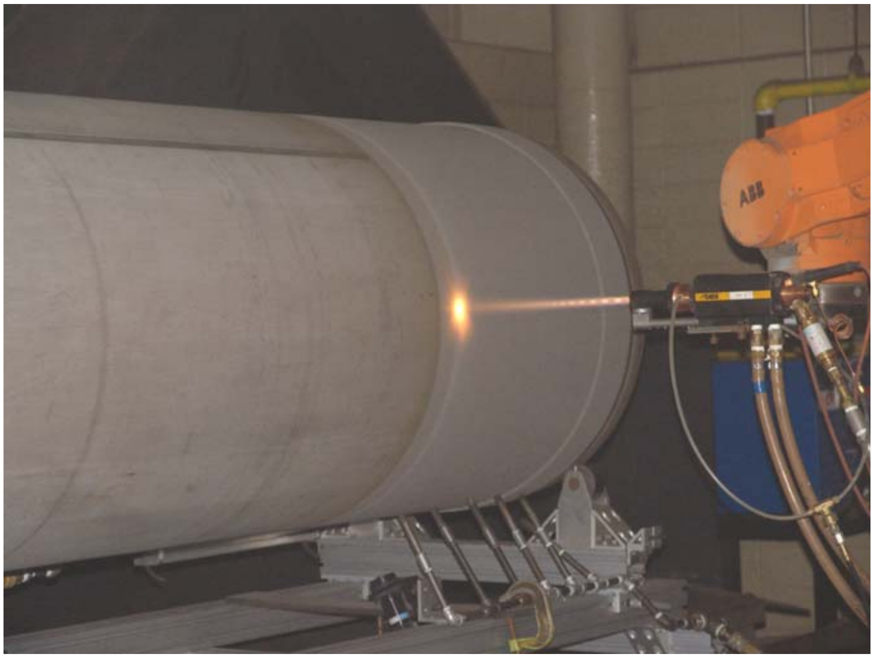


Figure 4.1-1. Spraying of the first section of the container is shown.

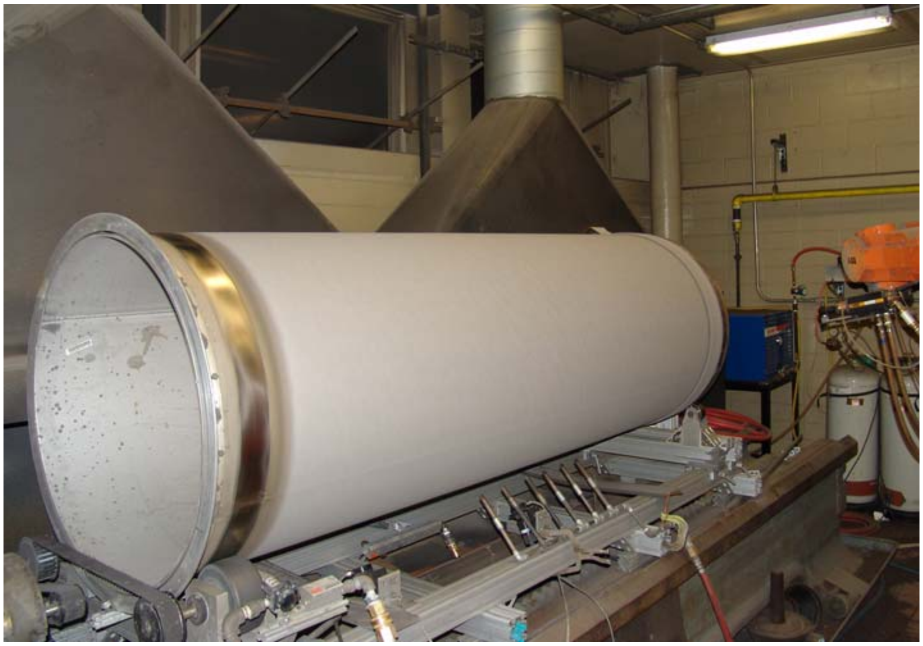


Figure 4.1-2. The first container with the OD coating completed is shown.

particles during spraying. After approximately one hour, the roughness of the ID has increased to the extent that the powder particles begin to deposit on the ID resulting in distortion of the flame and eventual plugging of the ID. The spray process was therefore stopped every hour to refill the powder hopper and change the torch barrel. This interruption could be as short as 15 minutes, but due to the extended time of spray, approximately 56 hours, there were numerous overnight stoppages as well.

4.1.1 Coating Defects

In addition to the interruptions due to powder and torch issues, failures of the fixture caused interruptions during actually spraying that resulted in defects being created in the coating. Two failures resulted in coating defects and were due to shaft failures that rotated the container resulting in the torch impinging on the coating for enough time to cause coating spallation or to melt the coating, Figures 4.1.1-1 and 4.1.1-4. Sensors were added after the second defect incident that detected the rotation of the container and moves the torch away when the rotation speed drops. This system has prevented any additional defects in the containers spraying to date.

(a)

(b)

(c)

Figure 4.1.1-1. First defect area caused by torch traversing on container without container rotating. Just after the torch was removed, the area was discolored (a) then started to crack as the container cooled (b). The cracked coating was chipped off for repair (c).

(a)

(b)

Figure 4.1.1-2. First defect area after blast was measured for roughness and found to be with specified range (a). The OD area of the defect was sprayed with 0.5 mm of coating prior to continuing to spray the entire length of the container OD (b).

The first defect occurred with approximately 0.774 mm of coating on the container and was approximately 1220 mm from the witness ring. Due to the cracking and spalling of the damage area, this defect was repaired by removing the loose coating and re-blasting the damaged area, Figure 4.1.1-1c and 4.1.1-2a. The entire diameter was sprayed the length of the defect with 0.5 mm of coating initially after which the coating of the entire length was continued, Figure 4.1.1-2b. The second defect occurred with approximately 1.597 mm of coating on the container and was 635 mm from the witness ring end, Figure 4.1.1-3. As the second defect did not spall as the first and resisted attempts to chip the damage area away, this defect was left intact and blasted and sprayed similar to the first, Figure 4.1.1-4.

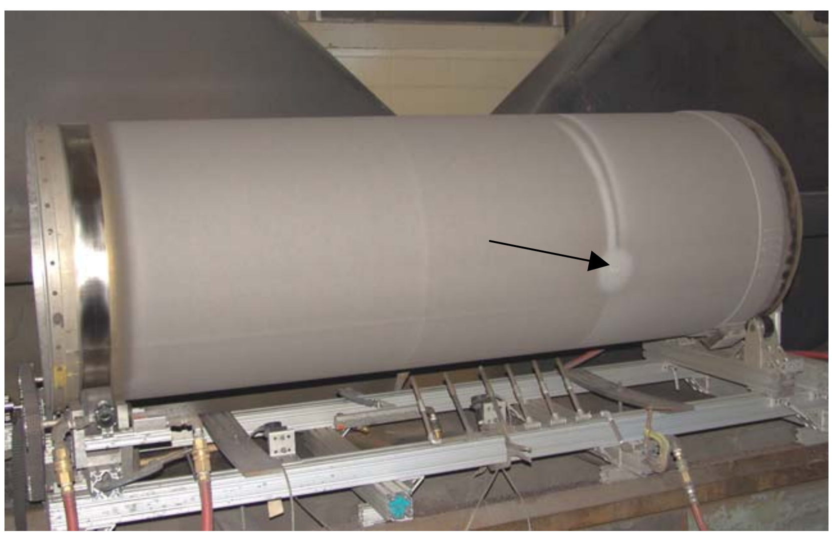
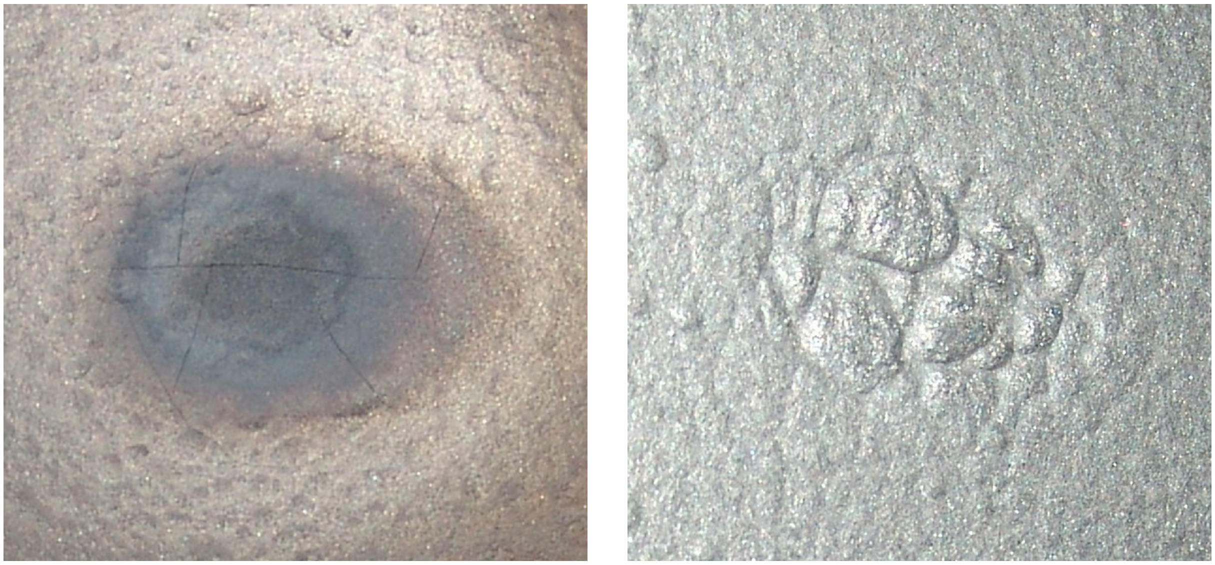


Figure 4.1.1-3. The location of the second defect area in relation to the witness ring is shown.



(a) (b)

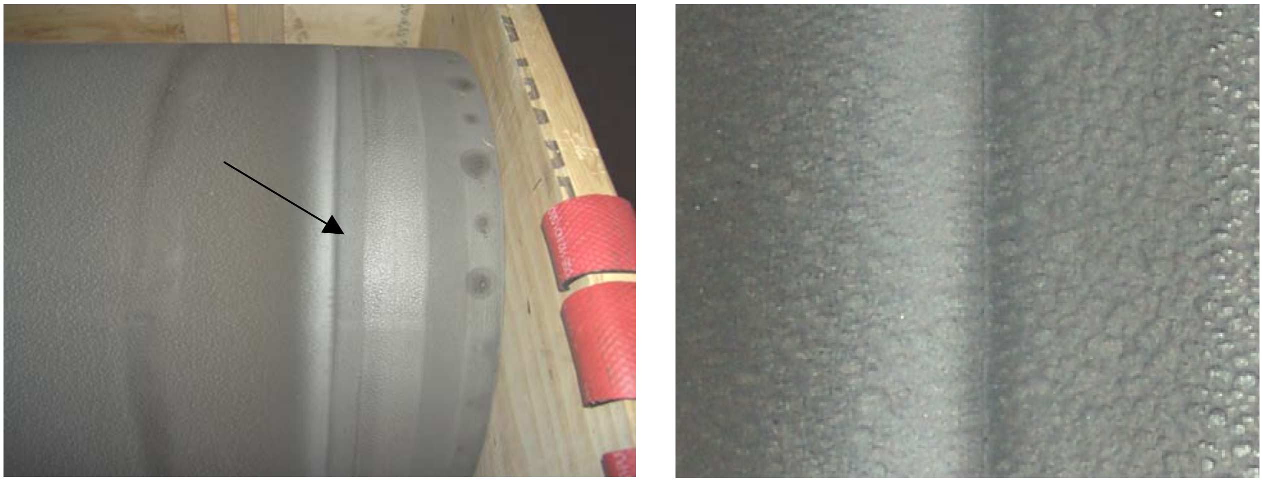
Figure 4.1.1-4. Close ups of the second defect before (a) and after the grit blasting (b). The grit blasting removed the cracked surface oxide and exposed what appears to be melted coating.

4.1.2 Witness Ring and End Spraying

The first section sprayed included the 100 mm wide witness ring that was clamped to the OD, Figure 4.1.2-1. The torch was angled 6º from normal in an attempt to shadow the corner of the ring in order to minimize entrapment in this zone. This torch angle was not sufficient and a large step was created at this location that resulted in a line “defect” around the OD of the container, Figure 4.1.2-2. The coating at the end of the container that did not have the witness ring did not exhibit this step. The area where the OD and end coatings were “tied” on the second end did not exhibit any defect, Figure 4.1.2-3. The spray procedure for the second container was changed by chamfering the witness ring to eliminate the coating build up or step at the witness ring.

(a) (b)

Figure 4.1.2-1. The witness ring for the OD on the first container (a) was not chamfered which created an area that caused the coating to be built up next to it (b).



(a) (b)

Figure 4.1.2-2. Area on first container showing defect line created by built up at witness ring (a). A close up of the line defect created is shown in (b).

(a) (b)

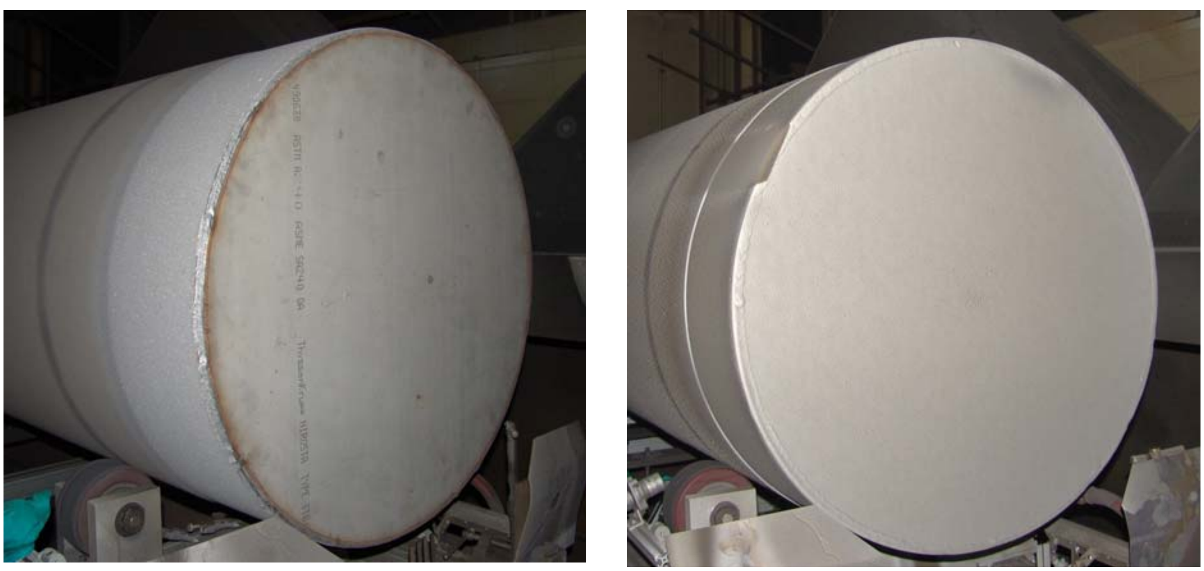
Figure 4.1.2-3. Area on first container showing smooth transition area on seconded end sprayed that did not have the witness ring attached (a). A close up of the transition line created is shown in (b).

The OD area that was covered by the witness ring was sprayed with the end of the container. The coating was alternately sprayed on the OD and end after 0.5 mm of coating thickness buildup, Figure 4.1.2-4. The torch was angled 45º to the OD as the corner of the container was approached to insure adequate coating build up, Figure 4.1.2-5. The end OD area was sprayed in a similar manner to the rest of the OD, while the flat end was sprayed with the container stationary and the torch moved in a raster pattern. The torch speed of movement was 1500 mm/sec (90 m/min). This is 18% slower than the surface speed of the OD of the container during spraying. The slower raster speed was used due to robot speed and acceleration limitations as well as the stability of the fixturing used to hold the torch. The raster step was 6 mm and was shifted by 2 mm after each completed raster pattern. The orientation of the container end to the raster pattern was random depending on where the rotation stopped after spraying of the OD. To speed the spraying of this end, a cooling lance was used on the ID of the container to cool the backside, Figure 4.1.2-6. This eliminated the need to pause the spraying of the end to maintain temperature. Pauses were used during coating of the lid end (the container completely closed) in order to maintain the substrate temperature near the targeted temperature of 150º C. The maximum substrate temperature of 198ºC was recorded during spraying of this end. The need for pauses during spraying for cooling resulted in more powder being used to coat the last end than the first.

The first prototype was completed on August 23, 2006 and shipped to E-Labs for corrosion testing, Figure 4.1.2-7.

The amount of powder used to spray the first prototype to a thickness of 2 mm totaled 555 lbs. Three different lots of the SAM1651 material were used as follows:

a) 225 lbs of Lot V5773
b) 270 lbs of Lot V5774
c) 86 lbs of Lot V5793



(a) (b)

Figure 4.1.2-4. Coating was applied to the OD area (a) not sprayed due to being covered by the witness ring to 0.5 thickness then the end was sprayed to 0.5 mm thickness (b). Spraying was alternated between the OD and end every 0.5 mm thickness.

Figure 4.1.2-5. The corner of the container was ground to a 45º angle. The spray torch was angled at 45º from the OD as the corner was approached in order to keep the spray angle near 90º to the surface being coated.

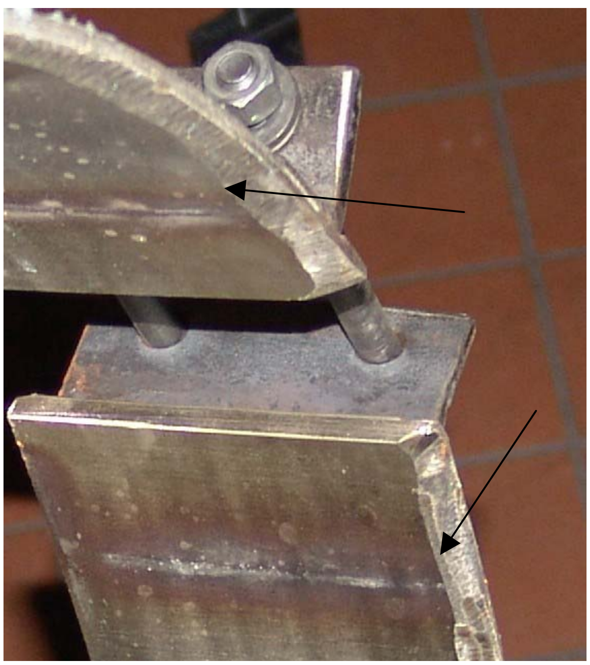
Figure 4.1.2-6. To aid cooling of the end during spraying, a cooling lance was used to provide for backside cooling. This could not be used for the lid end which resulted in longer spray time due to the need to pause for cooling.

Figure 4.1.2-7. First container crated for shipping.

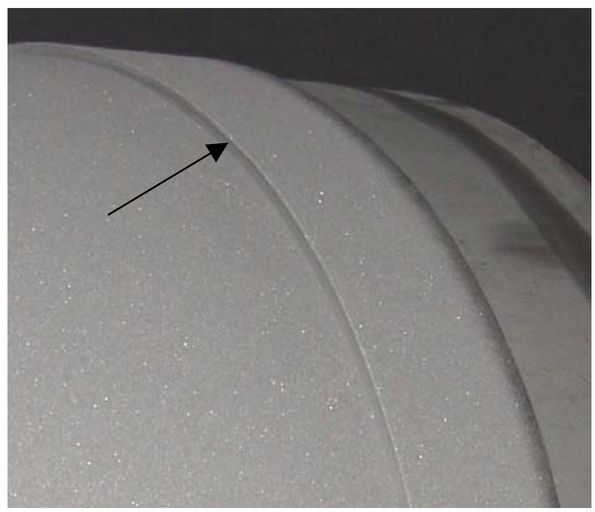
4.2 CONTAINER 2

The first container was sprayed to 2 mm thickness. The second and third containers will be sprayed to 1 mm thickness. Therefore approximately 280 lbs of powder will be required to spray the second container. Powder stock available at Caterpillar totals 370 lbs, so sufficient powder is on hand to complete the second container but an additional lot of material will be required to complete the third container. In addition, the need for initial qualification samples using the same lot of SAM1651 resulted in insufficient powder to complete the second container.

The second container was sprayed in a similar manner to the first container with three sections of the OD being first blasted and sprayed to ~200 micron thickness. The major change, in addition to the lower thickness, was the witness ring on the OD of the container was chamfered 45º to provided better shadowing to prevent buildup at the edge of the ring, Figure 4.2-1. In addition, the torch traverse speed was increased starting 25 mm from the ring and then slowed to the appropriate traverse speed once the spray area was on the ring sample. This was successful in removing the step in the coating and allowed a smooth transition to be created similar to that on the end without the witness ring.



(a)



(b)

Figure 4.2-1. The witness ring for the second container was hand-chamfered (a) to help create a better shadowing of the corner created on the container (b).

Spraying of the second container to 1 mm on the OD surface was completed on August 28, 2006. Spraying of the end surfaces on the second container was stopped in order to insure sufficient powder would be available to spray qualification samples.

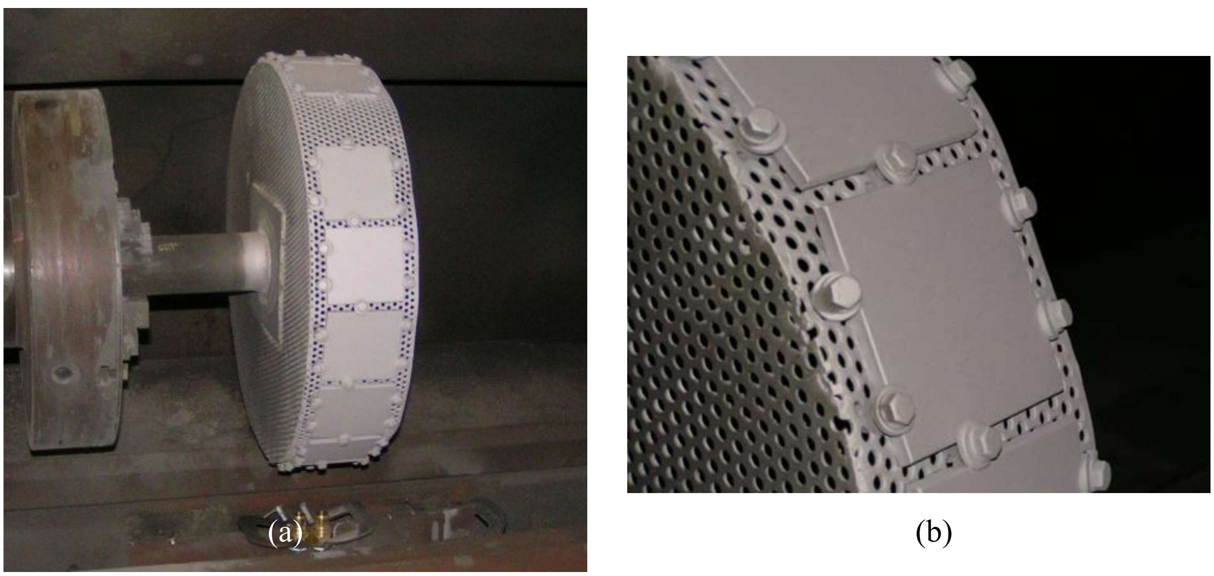
The amount of powder used to spray the second prototype to a thickness of 1 mm on the OD surface totaled 180 lbs. Only one lot of the SAM1651 material was used: V5793.

4.3 INITIAL QUALIFICATION SAMPLES

Initial qualification samples were sprayed for corrosion testing by the HPCRM team members. This was done under contract B559935, Deliverables 1, 2, 3, and 4. These samples were coatings of SAM1651 and SAM2X5 deposited on Type C22 alloy and Type 316 stainless steel. Two types of samples were coated, a 4” x 4” plate and a 0.75” diameter x 8.75” rod. Each substrate type was coated with both SAM1651 and SAM2X5.

4.3.1 INITIAL QUALILFICATION PLATES

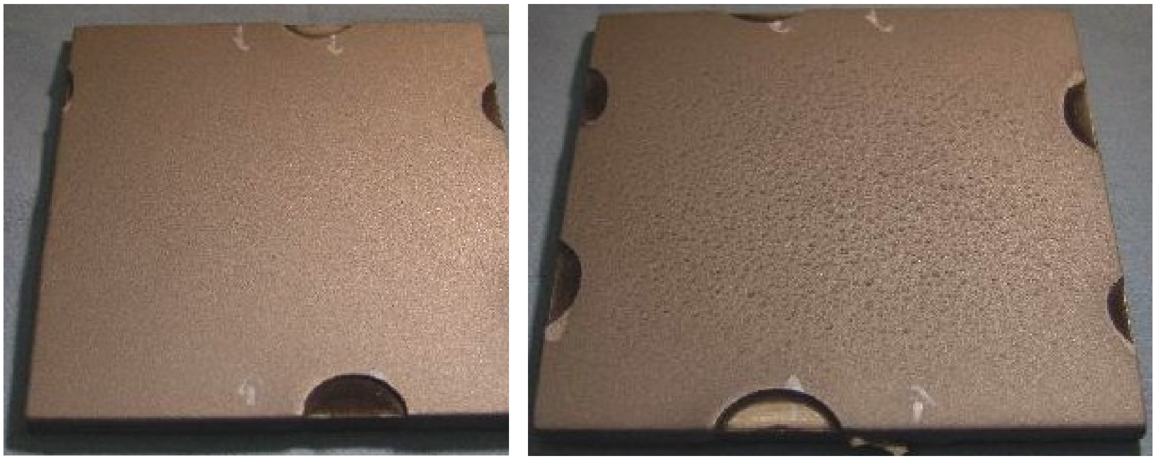
The plate substrate size for both SAM2X5 and SAM1651 coatings were 100 mm x 100 mm x 6.35 mm (4” x 4” x 0.25”). The samples were sprayed to a 1 mm thickness. Spray procedure used was similar to the spraying of the OD of the container with the samples mounted to a 711 mm (28”) wheel, Figure 4.3.1-1. The surface speed of the wheel was 110 m/min with a torch traverse of 6 mm per revolution, the same as used for the containers.



(b)

Figure 4.3.1-1. The initial qualification samples were sprayed in a manner similar to the containers with the specimens mounted to a 711 mm diameter wheel (a). Washers were used to mount the specimens on the wheel (b).

Each wheel setup held 17 samples. The samples were grit blasted after which one sample was removed as a witness plate of the grit blasting and replaced with a sample blasted by hand. The hand blasted sample was used to confirm the coating thickness after spray and one of the remaining samples was held as a witness sample. Fifteen samples from each drum setup were sent to LLNL as part of Deliverables 1 and 3 of contract B559935. As 60 samples of each type of substrate (C22 and 316L) were supplied for both powders, a total of 4 sets of wheels with 17 samples each were completed for each powder/substrate combination. The 240 samples have been sent to LLNL. Table 4.3.1-1 shows the panel identification with material used to produce each drum setup. Coating thickness aim was 1 mm on all the panels.



(a) (b)

Figure 4.3-2. Samples sprayed with the 130661 lot (a) of SAM1651 exhibited smoother as-sprayed surfaces than those sprayed with the V5773 or V5973 lot (b).

Table 4.3.1-1. 100 x 100 x 6.35 mm panels sprayed with 1 mm thick coatings were produced as shown. Parameters used to spray the samples are shown in Table 2-1.

Substrate	Powder	Run ID	Powder lot#	Quantity Shipped
316	SAM 1651	06-0925-E-1	V5793	15
316	SAM 1651	06-0925-E-2	V5793	15
316	SAM 1651	06-0925-E-3	V5793	15
316	SAM 1651	06-0926-E-1	V5793	15
		TOTAL		60
C-22	SAM 1651	06-0926-E-2	V5793	15
C-22	SAM 1651	06-0927-E-1	V5793	15
C-22	SAM 1651	06-0927-E-2	V5793	15
C-22	SAM 1651	06-0927-E-3	V5793	15
		TOTAL		60
316	SAM 2x5	06-0921-E-1	06-015	15
316	SAM 2x5	06-0921-E-2	06-015	15
316	SAM 2x5	06-0921-E-3	06-015	15
316	SAM 2x5	06-0922-E-1	06-015	15
		TOTAL		60
C-22	SAM 2x5	06-0928-E-2	06-015	15
C-22	SAM 2x5	06-0928-E-3	06-015	15
C-22	SAM 2x5	06-0928-E-4	06-015	15
C-22	SAM 2x5	06-0928-E-5	06-015	15
		TOTAL		60

In order to match the same cooling characteristics for the wheel setup versus the container spraying, a trial run was made using lot 130661 of SAM1651. The 130661 lot of powder had been produced in effort to determine how to make the SAM1651 material flow better. Surprisingly, samples sprayed with this lot of material exhibited a much smoother as-sprayed surface roughness than the samples sprayed with lots V5773 and V5973, Figure 4.3.1-2. The cause for this is not totally understood and further analysis of the higher roughness surfaces is provided in Section 4.4.1.

4.3.2 INITIAL QUALILFICATION RODS

Rod samples that were 19.05 mm diameter by 222.25 mm (0.75" dia. By 8.75") long were sprayed for Deliverables 2 and 4 of contract B559935. The rod length and one end were sprayed and approximately ¾ inch of one end was end left uncoated to allow for electrical connections during testing. A schematic of the rod geometry is shown in Figure 4.3.2-1. The rods were sprayed using the same spray parameters as the containers but with a different procedure due to the small rod diameter. Description of the procedure used to spray the rod specimens of C22 and 316L stainless steel follows:

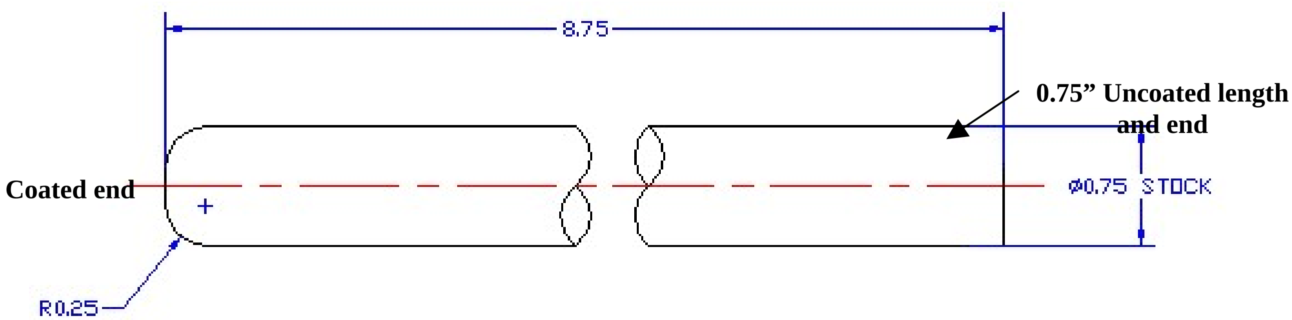


Figure 4.3.2-1. Schematic of the rod geometry sprayed for Deliverables 2 and 4.

4.3.2.1 Fixture and spray gun motion

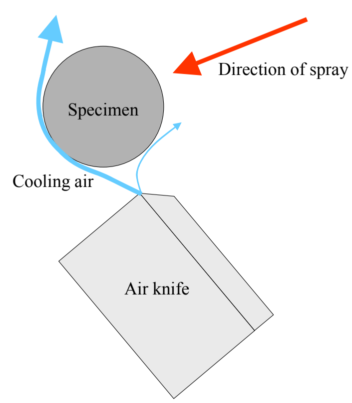
Specimens were rotated in two high-speed lathes to achieve surface speed comparable to the waste package coating process of 120 m/min (2005 RPM). Two lathes were used to allow alternating spray between the two to reduce heat build up, Figure 4.3.2.1-1. The rods were coated by a combination of a series of passes over the rod OD (torch perpendicular to the rod axis) and a raster motion over the free ends (torch oriented along the rod axis). The two motions (perpendicular to rod and raster on end) were alternated after 3 pass for the SAM1651 or 5 pass for the SAM2X5 so the coating layers overlapped at the transition from the OD of the rod to the radius on the end. The different number of passes were required for the two materials due to their different laydown rates per pass. The rod diameter of 19 mm is comparable to the width of the particle stream at 330 mm stand-off distance. A portion of the particles, located in the marginal area of the flame, impact at a lower angle than 90 degrees which results in lower deposition rate as compared to deposition on a flat surface with the same spray parameters. The smooth surface texture of the rod specimens of SAM1651 compared to the flat panel specimens is thought to be due to the low angle of impingement of most of the spray stream.

Figure 4.3.2.1-1. Spray fixture setup used for the rod samples is shown. Two rods we re sprayed at a time with the torch alternating between the rods to allow for cool down time.

4.3.2.2 Cooling and substrate temperature – material and fixture aspects

The time for the torch to pass over the rod specimens is significantly shorter than in the case of the spray packages or 4×4" plates, which would result in a higher substrate temperature if there is no delay between passes. Long delay between passes increases the wasted powder feedstock excessively; therefore, two lathes were used to coat two samples at a time. Without using a delay between passes, the substrate temperature was kept at acceptable levels by spraying the two samples at a time combined with a high pressure air cooling. Since there is only a small area coated during the raster deposition on the free end of the sample, the heat input is lower than during the OD spray as well. Smaller number of passes on OD before a change to deposition on the free end lowers the peak temperature. The motions on the OD and the free end were alternated after 5 passes for the SAM2X5 materials and after 3 passes for the SAM1651 since, at the given spray parameters, there is more heat input when using the SAM1651 material.

The cooling air-knife was directed at the specimen in a way that almost all the air passed on the side opposite to the spray torch, Figure 4.3.2.2-1. In this way, the stream of cooling air did not significantly affect the spray particles.



(a) (b)

Figure 4.3.2.2-1. Air cooling setup used to cool each rod is shown. The majority of the air flow was directed to the back side of the rod in order not to interfere with the HVOF spray stream.

4.3.2.3 Coating deposition on rods

The target spray parameters are listed in Table 4.3.2.3-1, column 2 and 3. The difference in lay-down rate between the SAM2X5 and SAM1651 at the given spray torch parameters is significantly smaller than in case of the deposition on 100 x 100 mm plates, column 4 and 5. Volume of deposited coating per unit time is calculated from the motion parameters, number of passes and the target thickness, Figure 4.3.2.3-1. The difference between the deposition rates on 19 mm rods vs. 100 x 100 mm plates can be attributed to the smaller dimension of the rods. There is a higher ratio of deposition rates for SAM1651 and SAM2X5 sprayed on 100 x 100 mm plates, which indicates a difference in the deposition mechanism on large flat vs. small/round surfaces. The SAM1651 coatings on the rods were almost “speckle-free” as opposed to a typical SAM1651 deposited on a large flat surface at the current parameters (except for the lot #130661, spray log 06-0923-E-1).

Table 4.3.2.3-1. Spray parameters for 19 mm diameter rods and 100 x 100 mm qualification plate specimens are shown for the SAM2X5 and SAM1651 coatings.

	06-0919-E-1 – 06-0928-E-5		06-1023-E-1 – 06-1101-E-7		
	0.75”Ø SAM2X5	0.75”Ø SAM1651	4x4” SAM2X5	4x4” SAM1651	
Fuel	25.7	28.4	25.7	28.4	L/hr
Oxygen flow	873	897	873	897	L/min
Stand-off	330	330	330	330	mm
Feed rate	75	75	75	75	gm/min
Carrier gas flow	10	14	10	14	L/min
Vibrator pressure	30	30	30	30	PSI
Traverse speed on OD	138	134	6	6	mm/s
Rotational speed	1385	1338	60	60	RPM
Surface speed	1388	1342	1995	1995	mm/s
Number of passes	118	120	122	103	
Target Thickness	0.95	0.95	1	1	mm
Lay-down rate	8.1	7.9	8.2	9.7	μm/pass
Area covered per time	8259	8020	11969	11969	mm^2/s
Volume of coating per time	66	63	98	116	mm^3/s
Powder lot used	06-015	V5793	06-015	V5793	

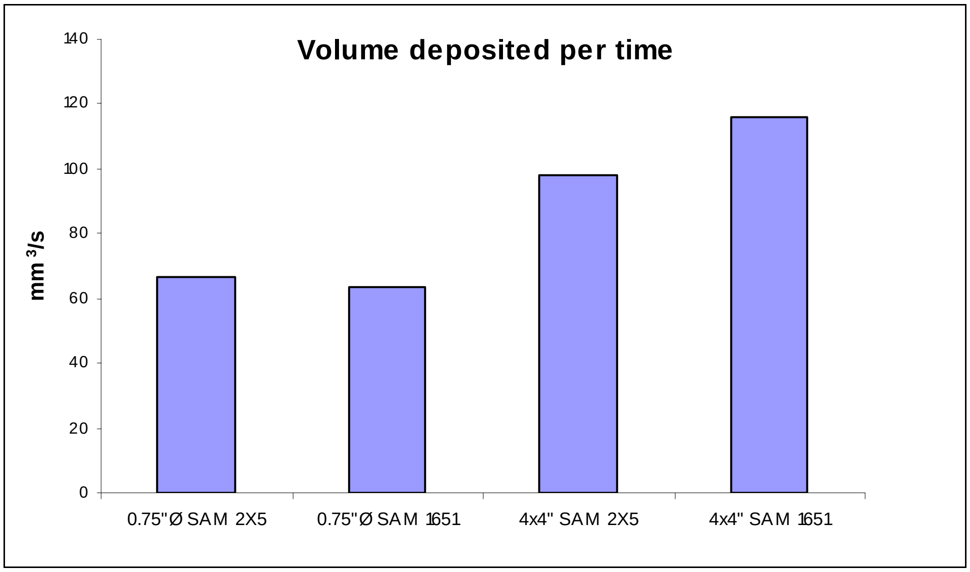


Figure 4.3.2.3-1. Volume of coating deposited per unit time

4.4 COATING MORPHOLOGY

Microstructure, composition and corrosion resistance of the SAM1651 4×4-inch qualification samples have been examined with respect to deposition conditions and feedstock particle size. The microstructures were characterized using light and scanning-electron microscopy (LEO 1550). Elemental composition data were obtained using an EDS detector (Oxford 6901) attached to the SEM. The corrosion test was performed according to ASTM B117 and the samples examined visually after 24, 48, and 120 hours.

The microhardness data and salt spray corrosion resistance were correlated with coating microstructure and a possible mechanism for the speckle formation is suggested.

Four sets of SAM1651 qualification specimens were analyzed and the deposition conditions are summarized in Table 4.3.2.3-1 and powder size information is shown in Table 4.4-1 and Figure 4.4-1. The runs 06-0925-E-1 and 06-0925-E-2 were performed under identical conditions. Powder particle size distributions are shown in Figure 4.4-1; the V5793 lot was characterized prior (P) to re-screening and after (F) re-screening at Carpenter. The powder was re-screened in an effort to avoid torch barrel loading and powder flow issues. The cooling setup contained two air nozzles covering the whole width of the plates directed at the coated side. Only one set of air nozzles was used for the runs 06-0922-E-1 and 06-0922-E-2 and the temperature was considerably higher; beginning with the 06-0923-E-1 run, an additional set of nozzles was added.

Table 4.4-1. Additional deposition conditions of the four sets of qualification samples analyzed.

Run ID	Powder lot	Median particle size (μm)	Cooling	Max substrate temperature (°C)
06-0922-E-2	V5793	40.1	Low	195
06-0923-E-1	130661	50.5	High	166
06-0925-E-1	V5793	40.1	High	168
06-0925-E-2	V5793	40.1	High	168

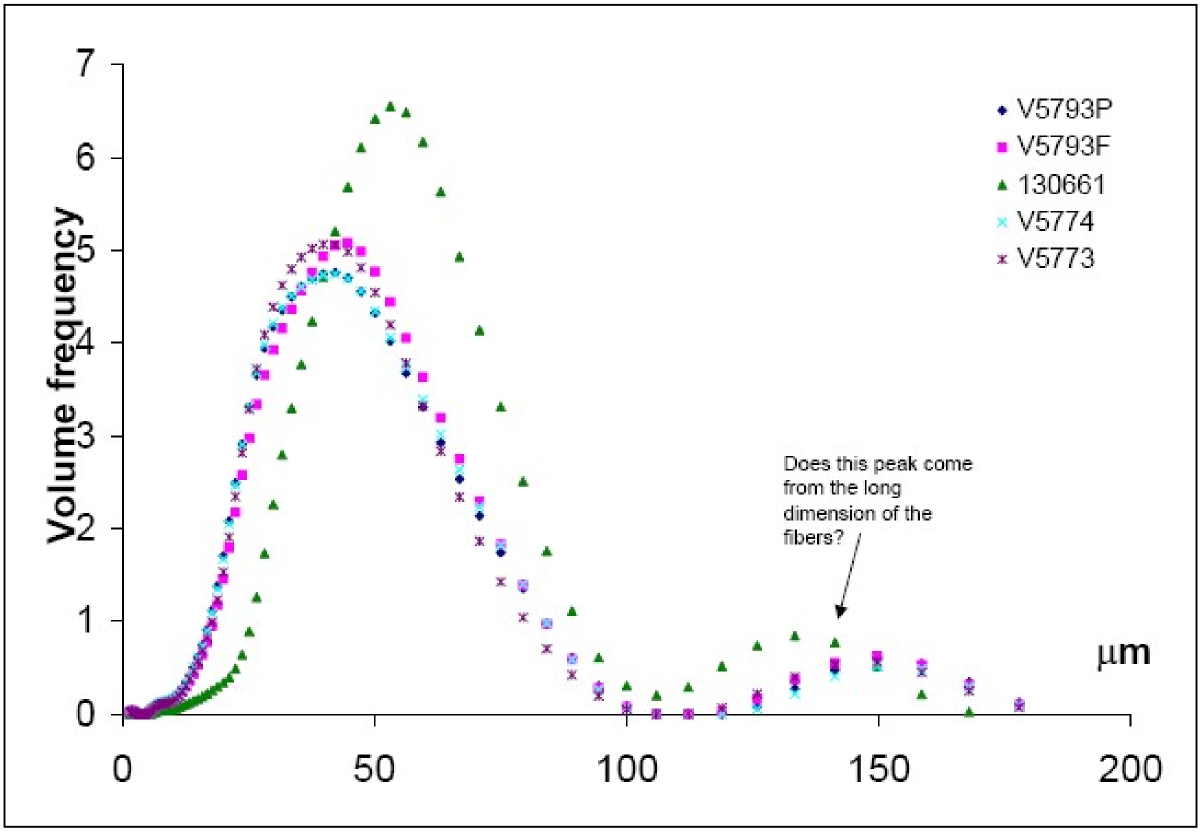


Figure 4.4-1. Particle size distribution (MicroTrac) of SAM 1651 powder lots used for qualifications samples and/or sub-scale package model.

4.4.1 POWDER LOT EFFECTS ON SPECKLE FORMATION

Speckles have been observed on all SAM 1651 samples, Figure 4.4.1-1, except those sprayed with 130661-powder lot, Figure 4.4.1-2, which had a larger mean particle size. The cross-sectional view of the speckle microstructure contains a large amount of porosity, Figure 4.4.1-3. It is not clear whether the porosity is a result of particle pull-out during polishing or is a true as-sprayed porosity. Vickers hardness through the speckle exhibits higher variation compared to the microstructure outside the speckle, Figure 4.4.1-3b; however, the mean hardness remains similar. The small difference in mean hardness values, HV at 500g load is 734±55 outside the speckle and 731±91 within the speckle, indicates that the porosity on the polished cross sections may actually be particles pull out during polishing, e.g. brittle oxides.

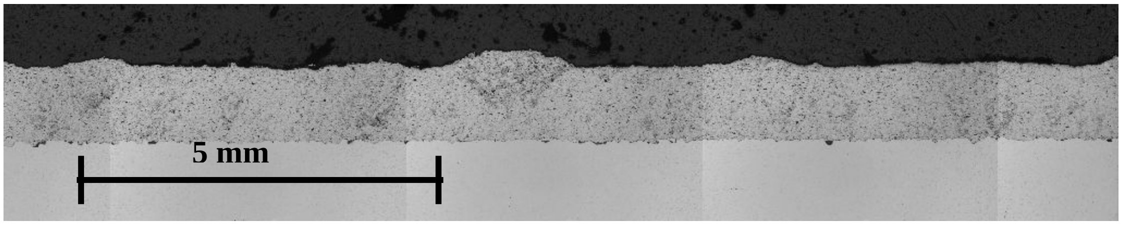


Figure 4.4.1-1. A speckle microstructure in the specimen 06-0925-E-1

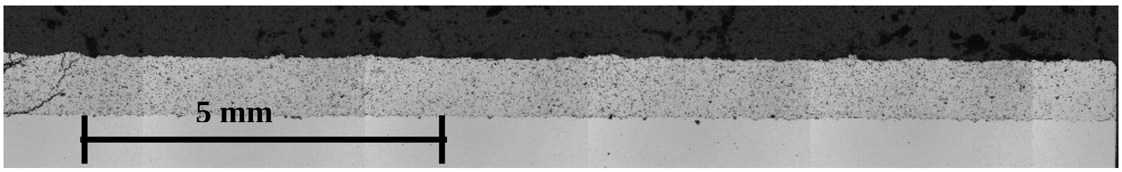


Figure 4.4.1-2. Microstructure of the speckle-free sample 06-0923-E-1 (large particle size distribution)

Oxygen content correlates with the void location within a speckle microstructure, Figure 4.4.1-4. A small, about 2 µm, globular particle present in the microstructure in Figure 4.4.1-4 may be a droplet splashed after impact of a larger molten feedstock particle. A two-micron particle is significantly smaller than a mean particle size of the feedstock (about 40 µm) and would be fully molten after traveling through the flame unless the trajectory leads through cold marginal parts of the flame.

The microstructure of the coating sprayed with the V5793 lot, outside the speckle, is similar to the microstructure of the coating sprayed with large particle size powder (06-0923-E-1, powder lot 130661), Figure 4.4.1-5. The hardness of the 06-0923-E-1 coating is lower compared to 06-0925-E-1 coating, HV (500gf) 683±140 and HV (500gf) 734±55 respectively, which indicates that the density is lower.

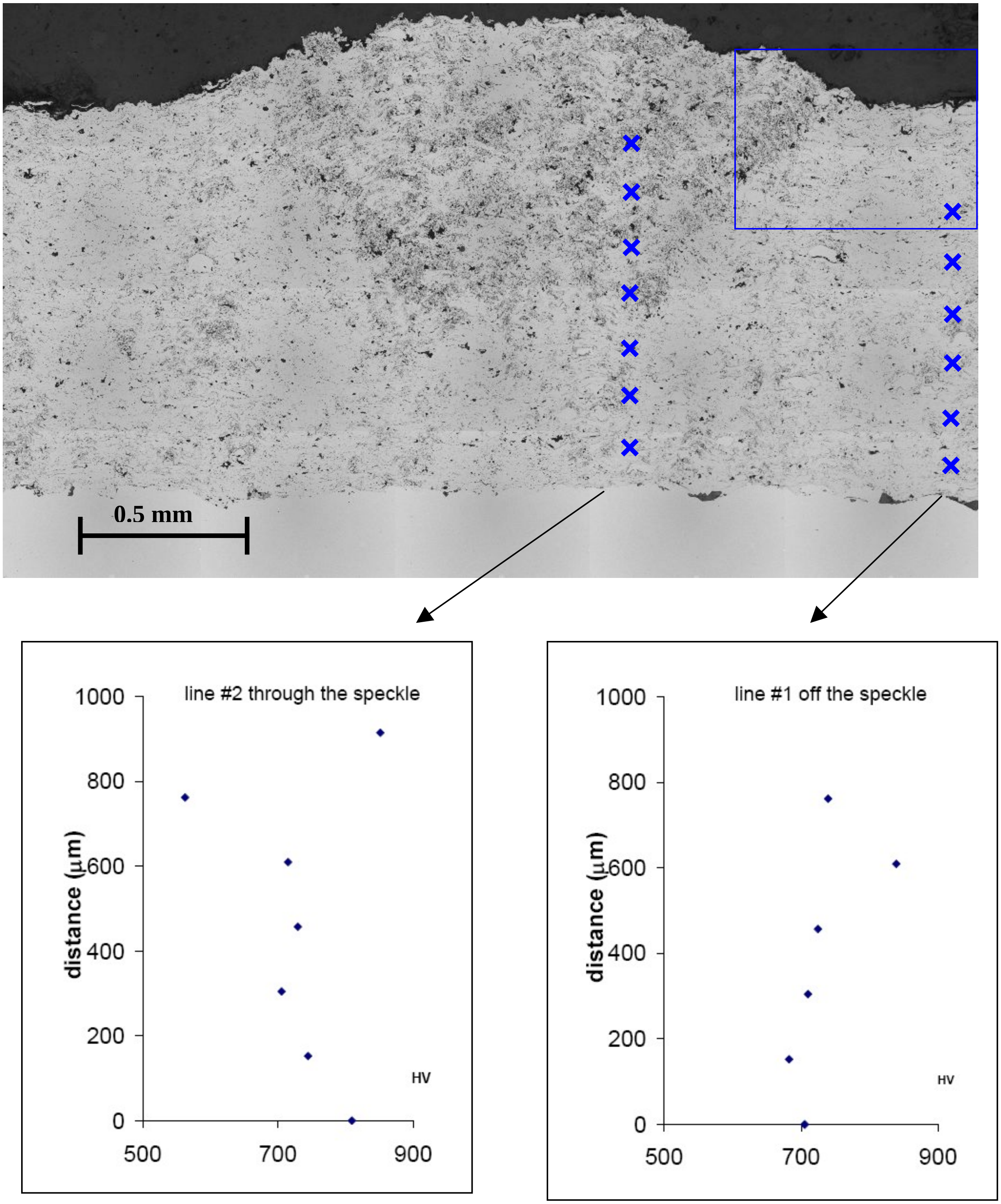


Figure 4.4.1-3. Cross sectional view of a speckle in the specimen 06-0925-E-1 with Vickers hardness measures taken as indicated in the oxidized pimple area and non-oxidized coating structure.

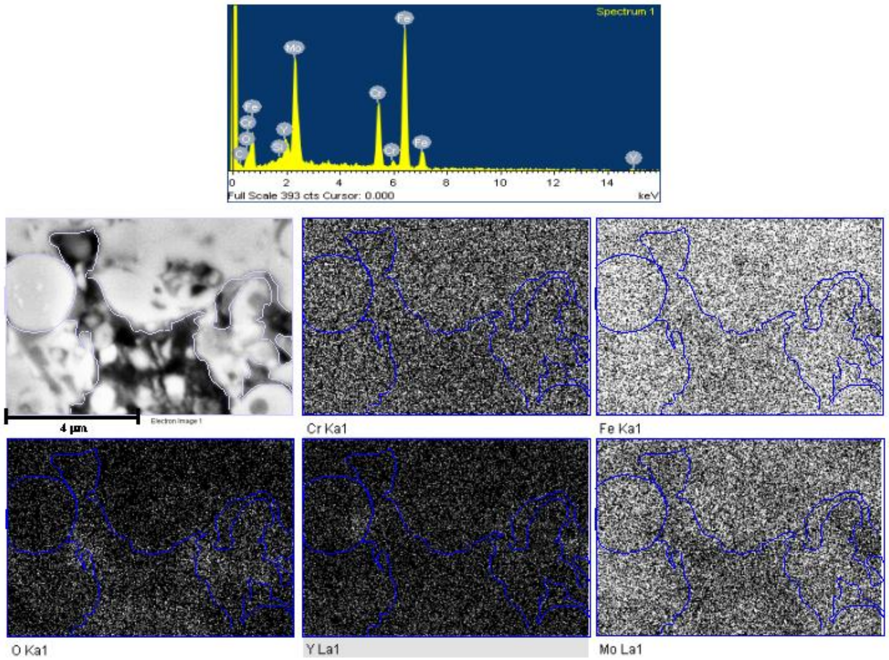


Figure 4.4.1-4. Elemental map of a detail microstructure within a speckle in the specimen 06-0925-E-1

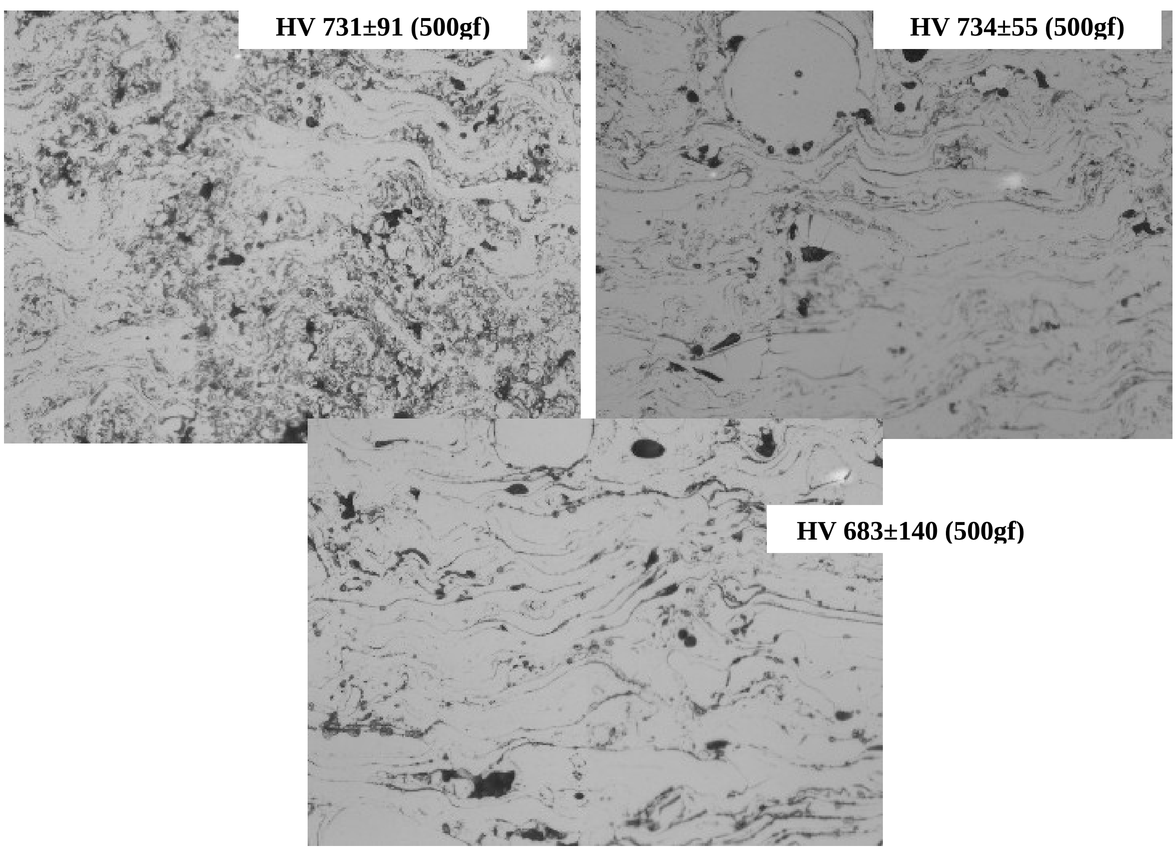


Figure 4.4.1-5. Side by side microstructure comparison; a) 06-0925-E-1 within the speckle, b) 06-0925-E-1 outside the speckle, c) 06-0923-E-1 (speckle free)

4.4.2 Possible mechanism of speckle formation

Porosity and oxide streaks are present at the edge of speckles, Figure 4.4.2-1. The spacing of the streaks is about twice the thickness of a single coating layer. A mechanism explaining the speckle formation that involves splashed molten droplets deposition is suggested.

When a molten or semi molten particle deposits on the substrate, small droplets detach and may be re-deposited on the substrate. The direction of droplet travel is probably in all directions in the half-space from the substrate but part of the droplets is ejected in a direction almost parallel to the substrate. The droplets are re-deposited on one side of an initial asperity of the coating, as the torch passes by, Figure 4.4.2-2a. Similarly, another layer of droplets is deposited on the other side of the asperity as the torch passes on that side, Figure 4.4.2-2b. The process repeats, until a wedge-shaped speckle is formed, Figure 4.4.2-2c-h.

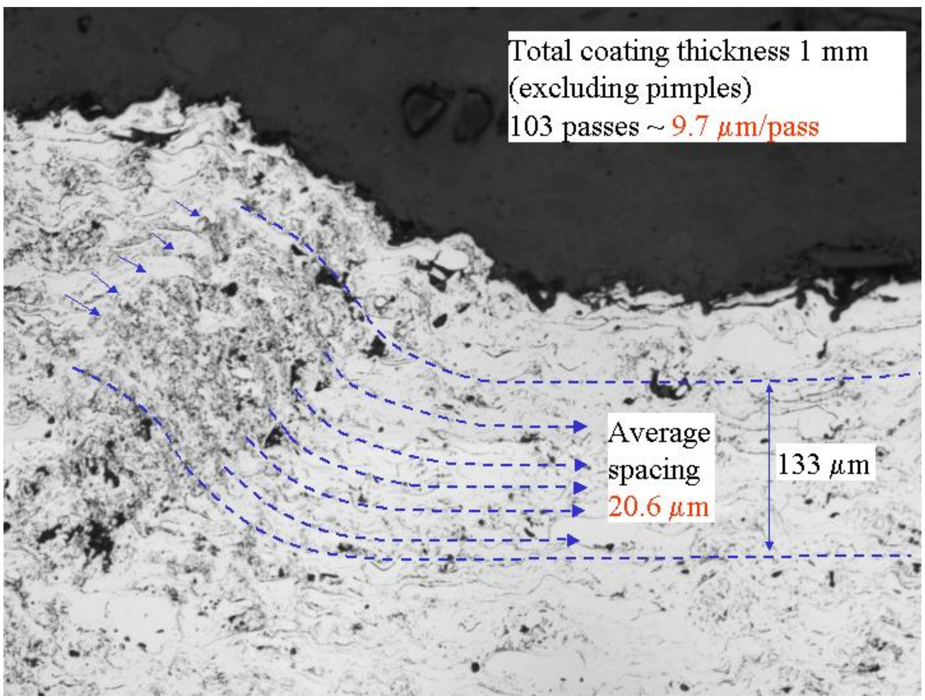


Figure 4.4.2-1. Oxide streaks within a speckle and its relation to deposition rate

4.4.3 Particle size and substrate temperature effects on coating corrosion resistance

The samples have been tested in a salt spray chamber and visually examined after 24, 48, and 120 hours. Rust spots were obvious after 120 hours period, Figure 4.4.3-1. The rust spots were larger on the 06-0922-E-2 and 06-0925-E-2 samples (V5793 lot); however there were many smaller spots on the 06-0923-E-3 sample (larger particle size). The corrosion appears to be associated with the speckles, Figure 4.4.3-2. It is not clear what defects are related to the corrosion spots on the speckle-free sample, Figure 4.4.3-2b.

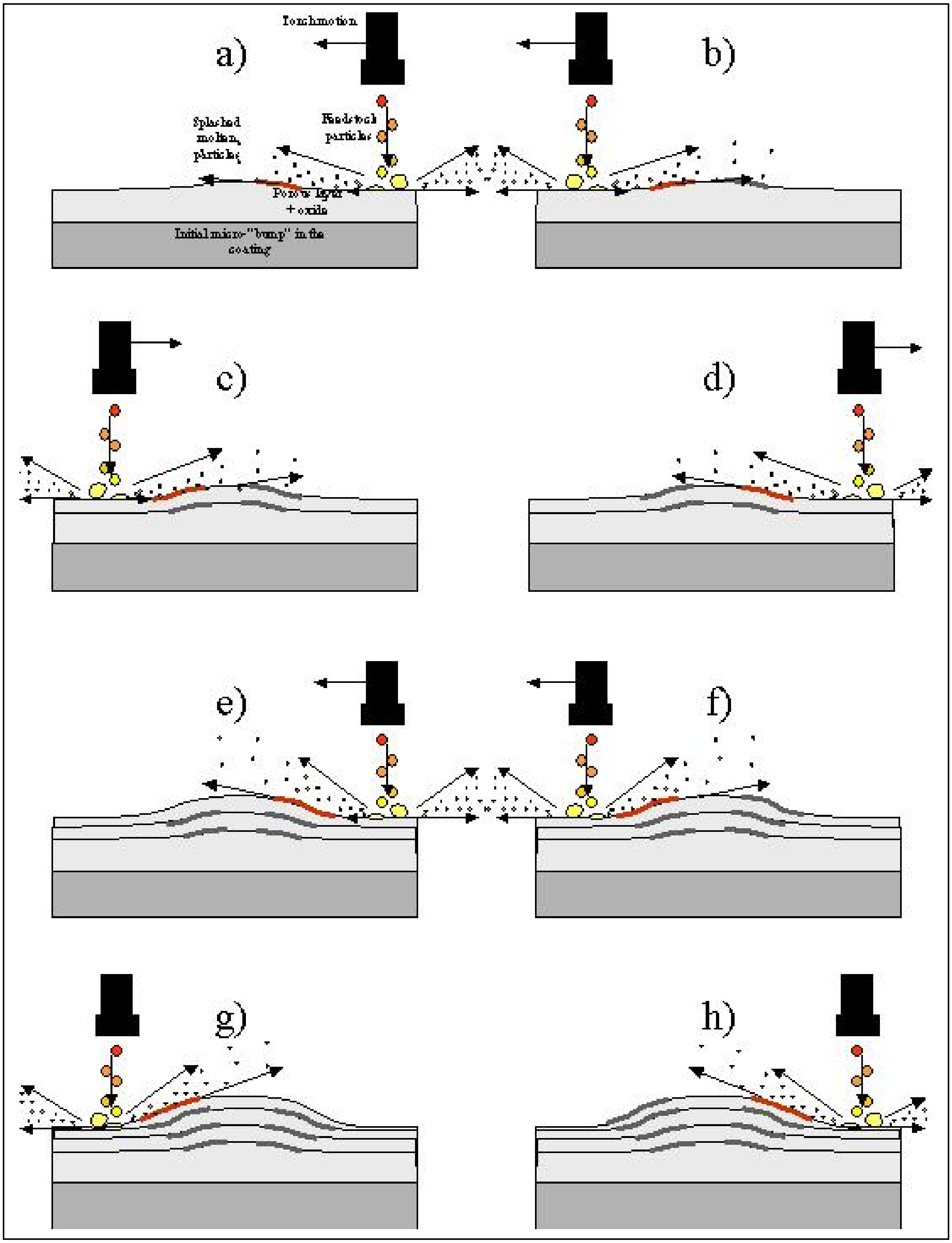
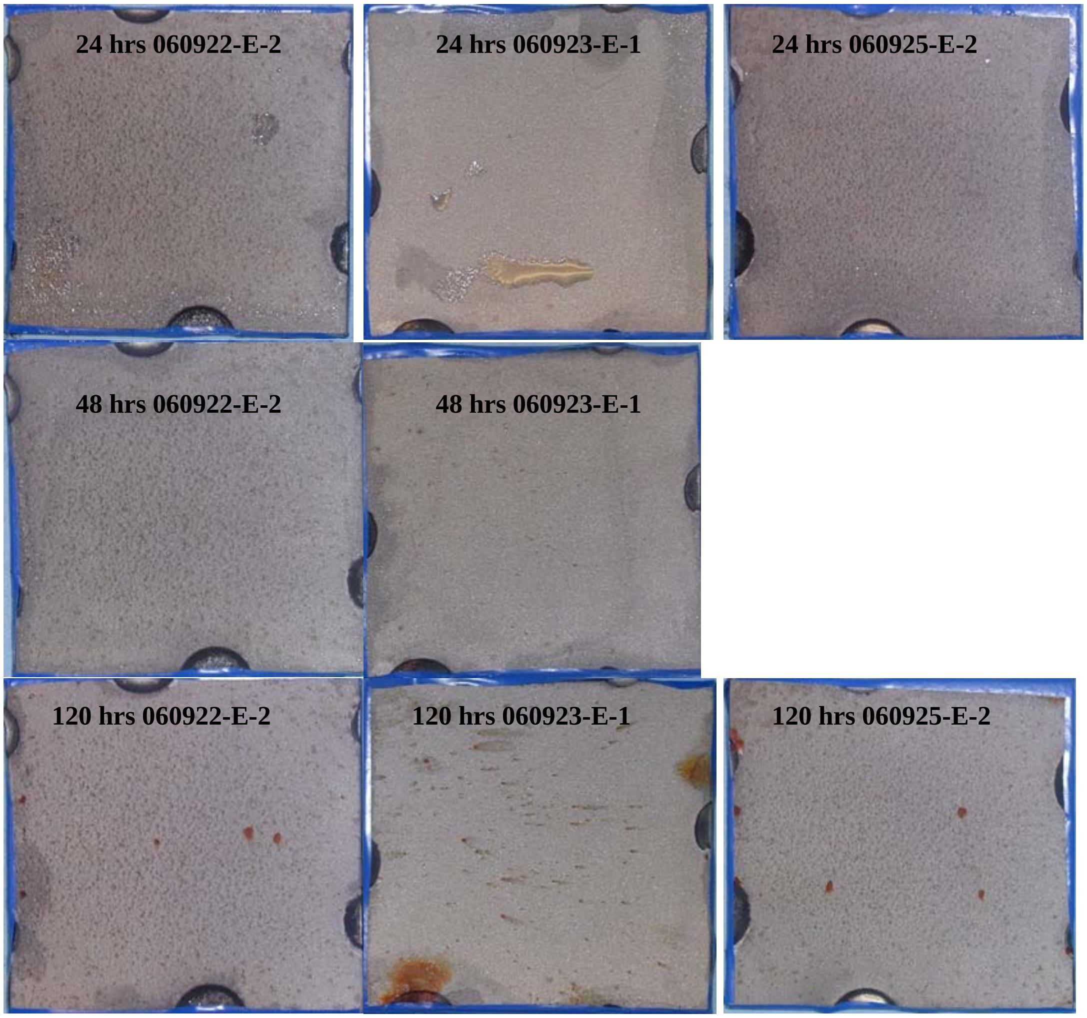
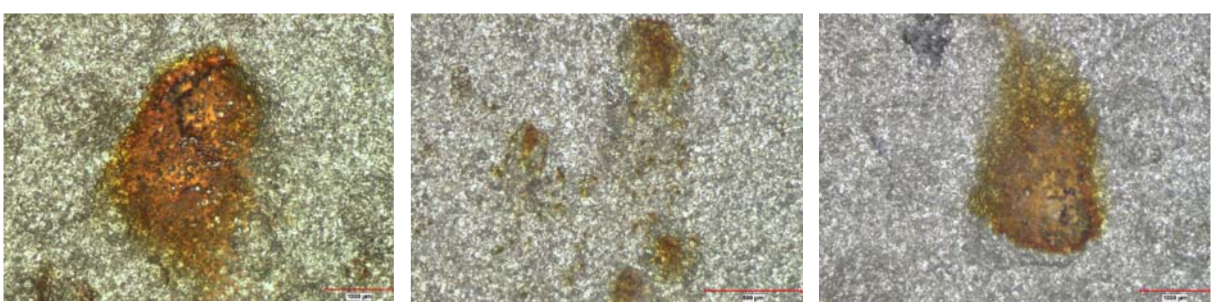


Figure 4.4.2-2. The suggested relationship of the oxide layers and the torch motion



(a) (b) (c)

Figure 4.4.3-1. Coating surface after salt spray test; a) lot# V5793 low cooling, b) lot #130661 - large particles size high cooling, c) lot# V5793 high cooling



(a) (b) (c)

Figure 4.4.3-2 Rust spots on tested samples; a) 06-0922-E-2, b) 06-0923-E-1 (speckle-free), c) 06-0925-E-2

In summary, the following trends were seen for the various powder lots:

- Larger feedstock particle size eliminates formation of large speckles on the coating surface
- Larger feedstock particle size does not eliminate corrosion of the coating
- Larger feedstock particle size results in a somewhat lower hardness and probably density as well, which may have a negative impact on corrosion resistance
- Deposition parameters should be optimized to achieve a speckle-free coating while maintaining low porosity.

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5. THERMAL SPRAY STANDARD

In order to provide high quality thermal spray coatings, processes must be developed and documented that will reliably produce acceptable results. A standard document is being drafted that identifies, in detail, the necessary process steps. The Standard also details the inspections needed to confirm that the processes have actually been performed according to the Standard. The development of a database to record the inspection findings has been initiated.

5.1 DRAFT STANDARD

No DOE thermal spray standards that can be widely disseminated have been identified. Therefore, the content of two Navy thermal spray standards, MIL-STD-1687A and MIL-STD-2138A, has been adapted for Department of Energy (DOE) use. The focus of this DOE draft Standard is thermal spraying of High Performance Corrosion Resistant Materials (HPCRM) available in powder form (not wire). Because the specific process parameters are presently being developed, the Standard is a living document that will adapt itself as the HPCRM research program evolves. The goal is to have a thorough, but user-friendly, document ready if and when thermal spray HPCRM is applied commercially to DOE components. This Standard will comprise a substantial part of the overall quality assurance (QA) program for use of HPCRM coatings in DOE.

While “best industrial practices”, when followed assiduously, can produce acceptable coatings, there is too much of an opportunity for processes to drift out of specification. This drift can be due to complacency, misunderstanding, or a desire to cut corners to meet cost or schedule. The Standard provides a very specific basis for the applicator (and even the customer) to avoid accepting out-of-specification conditions. The Standard is being written to include a series of process steps that must be performed in order to ensure high coating performance. Along with each process step, the appropriate inspection procedure is also presented as a checkpoint.

5.2 INSPECTION PROCEDURES

Inspection procedures have been derived from the Navy thermal spray standards, NACE International (formerly National Association of Corrosion Engineers) coating inspection procedures, and Navy Preservation Teams inspection protocols. Ensuring a high-quality coating involves ensuring that the procedure is properly documented for the specific task, avoiding contamination and moisture condensation, having an appropriate substrate roughness, proper powder conditions, good equipment condition, part cooling, and proper spraying parameters. Additionally, safety procedures must be followed. The inspection process is being developed to provide confirmation of all of these conditions.

The selection of the individual to perform the inspections is very important. In the ideal case, the inspector is “third-party”, a highly trained (NACE Certified) and experienced person whose responsibility is to the customer, not to the applicator, in order to avoid a conflict of interest. It behooves the applicator to also have an inspector (or inspection-trained foreman) who understands the perspective and expectations of the third-party inspector so that the job will be performed correctly the first time. This is particularly important in the present case because removing the coating in case of a deficiency is extremely difficult. The inspection procedures, covering all aspects of the job, will be spelled out in detail in the thermal spray Standard so that the customer, applicator, and inspector all know what is required. Because of the critical requirements for the product of this program, there must be 100% checkpoint attendance by the third-party inspector, monitoring applicator activities and spot checking measurements using the third-party inspector's own instruments.

5.3 INSPECTION DATABASE

In order to document every process step and highlight any deficiencies, an electronic database will be used by the inspector to record all findings required by the Standard. Being electronic, the database will be completely searchable at any time in the future. Searchability allows transparency, accountability, immediate recall of measurements and parameters, and trending of data. These trends can be a basis for revision of operating parameters and reducing or enhancing requirements. It is envisioned that there will be a master database that retains all program data and that has appropriate backup capabilities. To enhance functionality, this database will be a fully relational information system (such as Microsoft Access or Oracle). The input process for on-site inspectors is to be determined. A hand-held (PDA) or laptop computer nearby is needed. The process must be refined to avoid transcription errors (that could lead to false deficiency reports). The data input process should be linear, walking the inspector through each measurement or observation in order, so that nothing is overlooked. The inspector's data will be periodically uploaded to the master database (and retained by the inspector for local use and as another level of backup). The applicator may benefit by independently using this database as well.

5.4 THE DEVELOPER

Robert Bayles, a NACE-trained coating inspector, played a major role in the development of the Navy Preservation Teams coating inspection document. He developed a coating inspection database that has been accepted for commercialization by a Navy contractor. During these developments he performed coating inspections on Navy ships and submarines. During the development of the DOE Standard and database, Robert Bayles attended the spraying of DOE components at Caterpillar Company and incorporated the perspective gained by his on-site observations into the Standard and database development.

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6. CONCLUSIONS

1) Coating of prototype large-scale structures with HPCRM coatings has been demonstrated. Spraying of full-scale SNF/HLW containers will require the design of specialty part and/or torch manipulators to provide a reliable coating application process.

2) Second generation SAM1651 powders show improved powder flow and coating consistency. Further improvements will be required to provide the consistency in size distribution and morphology required for production spray processes for full-scale SNF/HLW containers. Elimination of the fibers in the SAM1651 should be given a high priority.

3) Torch hardware life for the TAFA JP5220 presents significant issues to development of robust, reliable spray process. Torch parameters and/or new torches should be investigated to increase component life to allow coating of at least one container without torch maintenance. Parameters that eliminate the "speckled or pimpled" oxide surface will also be needed.

4) Heat management issues to maintain coating/substrate temperatures at currently specified limits should be addressed in the design of a coating facility for full-scale SNF/HLW structures. Both the issue of spraying on the containers after final closure weld and the use of multiple spray torches to reduce total spray time will be significant challenges.

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7. FUTURE WORK

Future work to be completed as part of this contract (B559010) include:

1) Coating of the third container to a thickness of 1 mm.

The current powder inventory of SAM1651 material at Caterpillar is shown in Table 7-1. The quantities required to complete one end of the second container has been estimated to be 60 lbs of material. The estimate to complete third container with 1 mm of coating and with only one end coated (similar to the second container) is 275 pounds. With the limited quantities on hand, the third container cannot be completed with SAM1651. In addition, completing the second container using powder on-hand will limit the extent of work that can be done to understand the powder morphology and torch issues required to spray production SNF/HLW containers. Additional lots of SAM1651 material will be acquired to complete of the containers as well as provide additional powder to evaluate alternate torch hardware life issues.

Table 7-1. Inventory of SAM1651 powder at Caterpillar after completion of first container, spraying OD of second container, and completion of plate qualification samples

Powder	Lot#	Total Inventory, lb
SAM1651	130658	56
SAM1651	130659	70 (does not flow)
SAM1651	130660	60
SAM1651	130661	15
SAM1651	V5773	51
SAM 1651	V5774	15
SAM1651	V5793	32
SAM1651	V5060	20
SAM1651	V5060B	34
Total		**353**
Total powder the flows		**283**

In addition, further development of the powder and torch parameters for spraying SAM1651 is required to reduce and eliminate the “speckled or pimple” surface defect while maintaining dense coating structure for optimum corrosion resistance. The required development to meet these requirements is planned as part of contract B559935 prior to coating the final container for this contract.

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